

WHAT IS CLAIMED IS:

1. A thermoplastic polyurethane composition, comprising:
the reaction product of
a polyester polyol having a number average of molecular weight of from about 500 to about 5,000;
from about 1 to about 50 parts by weight of a polyether co-polyol comprising poly(tetramethylene ether glycol), poly(propylene oxide), poly(propylene oxide-co-ethylene oxide), polyethylene oxide or combinations thereof per 100 parts by weight of the total amount of said polyol;
a polyisocyanate having the formula $R(NCO)_n$ where n is an integer of from 2 to 4 and R is an aromatic, cycloaliphatic, aliphatic, or combinations thereof having from 2 to about 20 carbon atoms;
a symmetrical chain extender;
from about 1 to about 50 moles of a co-chain extender that is asymmetric or of a different chain length or is non-linear or contains a heteroatom co-chain extender per 100 moles of said symmetric chain extender;
the molar ratio of said co-chain extender to weight percent of said polyether polyol being from about 0.1 to about 10.
2. A thermoplastic polyurethane composition according to claim 1, wherein said co-chain extender comprises 1,3-butanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, di(β -hydroxyethyl) resorcinol or 1,2-propylene glycol, or combinations thereof; and
wherein said reaction product has a reduced annealing value, V_t , of about 4.0 or less and a sensitivity of the complex viscosity to temperature V_R $((T_m+15)/(T_m+35))$ of about 9 or less.
3. A thermoplastic polyurethane composition according to claim 2, wherein said symmetric chain extender comprises 1,6-hexanediol, 1,3-propanediol,

1,5-pentanediol, 1,4-butanediol, 1,4-cyclohexanedimethanol (CHDM), hydroquinone di(β -hydroxyethyl) ether (HQEE), or 1,4-benzenedimethylol, or combinations thereof;

wherein said reaction product has a sensitivity to shear V_f at $T_m+15^\circ\text{C}$ of about 10 or less or a V_f at $T_m+35^\circ\text{C}$ of about 5 or less;

wherein the amount of said polyether co-polyol is from about 2 to about 25 parts by weight per 100 parts by weight of said polyester polyol, and

wherein said molar ratio of said co-chain extender to the weight percent of said polyether polyol is from about 0.15 to about 3.

4. A thermoplastic polyurethane composition according to claim 3, wherein the number average molecular weight of said polyester co-polyol is from about 600 to about 4,000; and

wherein the number average molecular weight of said polyether polyol is from about 250 to about 5,000, and

wherein said reaction product has a hydrolytic stability, TS_N , of about 0.3 or greater.

5. A thermoplastic polyurethane composition of claim 4 wherein said polyether polyol is selected from the group consisting of poly(tetramethylene ether glycol), poly(ethylene oxide), poly(propylene oxide), poly(propylene oxide-co-ethylene oxide), and mixtures thereof.

6. A thermoplastic polyurethane composition of claim 5 wherein said co-chain extender is neopentylglycol, dipropylene glycol, 1,3-butanediol, or mixtures thereof.

7. A thermoplastic polyurethane composition according to claim 6, wherein said reduced annealing value V_t is about 3.5 or less, wherein said V_f at $T_m+15^\circ\text{C}$ is about 6 or less, and said V_f at $T_m+35^\circ\text{C}$ is about 4 or less, wherein said polyether polyol is poly(tetramethylene ether glycol), wherein said diisocyanate is

MDI or H₁₂MDI, or combinations thereof, wherein said symmetrical chain extender is 1,4-butanediol; and

wherein the molar ratio of said co-chain extender to the weight percent of said polyether polyol is from about 0.1 to about 10; and

wherein said co-chain extender is 1,3-butanediol, neopentylglycol, or dipropylene glycol.

8. A thermoplastic polyurethane composition of claim 7 wherein the molar ratio of said co-chain extender to the weight percent of said polyether polyol is from about 0.15 to about 3.

9. A thermoplastic polyurethane composition of claim 8 wherein the molar ratio of said co-chain extender to the weight percent of said polyether polyol is from about 0.2 to about 2.

10. A thermoplastic polyurethane composition according to claim 7, wherein said polyester polyol is derived from adipic acid, suberic acid, sebacic acid, or azelaic acid, or combinations thereof with 1,4-butanediol, 1,6-hexanediol, neopentyl glycol, diethylene glycol, or combinations thereof.

11. The thermoplastic polyurethane composition of claim 1, wherein said co-chain extender is used at a level of from about 5 to about 10 moles per 100 moles of said symmetrical chain extender.

12. The thermoplastic polyurethane composition of claim 11, wherein said polyether co-polyol is used at a level of from about 5 to about 20 parts by weight per 100 parts by weight of the total amount of said polyol.

13. A thermoplastic polyurethane composition wherein at least four of the following six (A through F) criteria are met:

A. a reduced crystallinity expressed as T_{CN} is 0.95 or less,

- B. an improved hydrolytic stability expressed as TS_N is 0.3 or greater,
- C. a reduced sensitivity to shear expressed as $V_f(T_m + 15)$ is 10 or less,
- D. a reduced sensitivity to shear expressed as $V_f(T_m + 35)$ is 5 or less,
- E. a sensitivity of the complex viscosity to temperature expressed as V_{ft} is 10 or less, and
- F. a reduced annealing expressed as V_t is 4 or less.

14. The thermoplastic polyurethane composition of claim 13 wherein at least five of the criteria (A through F) are met.

15. The thermoplastic polyurethane composition of claim 14 wherein all six of the criteria (A through F) are met.

16. The thermoplastic polyurethane composition of claim 13 wherein T_{CN} is 0.85 or less, TS_N is 0.35 or greater, $V_f(T_m + 15)$ is 6 or less, $V_f(T_m + 35)$ is 4 or less, V_{ft} is 9 or less, and V_t is 3.5 or less.

17. The thermoplastic polyurethane composition of claim 16 wherein at least five of the criteria are met.

18. The thermoplastic polyurethane composition of claim 17 wherein all six of the criteria are met.

19. A coated fabric wherein said coating comprises the thermoplastic polyurethane composition of claim 1.

20. A coated fabric wherein said coating comprises the thermoplastic polyurethane composition of claim 13.

21. A coated fabric wherein said coating comprises the thermoplastic polyurethane composition of claim 16.

22. A coated fabric wherein said coating comprises the thermoplastic polyurethane composition of claim 16, and wherein said fabric comprises nylon, polyester, or polyolefin.

23. A sheet or a film comprising the thermoplastic polyurethane composition of claim 1.

24. A sheet or a film comprising the thermoplastic polyurethane composition of claim 13.

25. A sheet or a film comprising the thermoplastic polyurethane composition of claim 16.

26. A sheet or film comprising the thermoplastic polyurethane composition of claim 17.

27. A conveyor belt comprising the thermoplastic polyurethane composition of claim 1.

28. A conveyer belt comprising the thermoplastic polyurethane composition of claim 13.

29. A conveyer belt comprising the thermoplastic polyurethane composition of claim 16.

30. A conveyer belt comprising the thermoplastic polyurethane composition of claim 17.

31. An inflatable article, an apparel, or a storage bag comprising the thermoplastic polyurethane composition of claim 1.

32. An inflatable article, an apparel, or a storage bag comprising the thermoplastic polyurethane composition of claim 13.

33. An inflatable article, an apparel, or a storage bag comprising the thermoplastic polyurethane composition of claim 16.

34. An inflatable article, an apparel, or a storage bag comprising the thermoplastic polyurethane composition of claim 17.

35. A process for producing a thermoplastic polyurethane polymer comprising reacting:

A. a polyester polyol having a number average molecular weight of from about 500 to about 5,000;

B. from about 1 to about 50 parts by weight of a polyether co-polyol per 100 parts by weight of the total amount of said polyol;

C. a polyisocyanate;

D. a symmetrical chain extender;

E. from about 1 to about 50 moles of a co-chain extender that is asymmetric or of a different chain length or is non-linear or contains a heteroatom co-chain extender per 100 moles of said symmetrical chain extender; and

wherein the molar ratio of said co-chain extender to weight percent of said polyether polyol is from about 0.1 to about 10.

36. The process of claim 35 further comprising a thermoplastic polyurethane catalyst in an amount less than about 1000 parts by weight per million parts by weight of the combined weight of said polyester polyol, polyether co-polyol, polyisocyanate, symmetrical chain extender and said co-chain extender.

37. The process of claim 36 wherein said process is conducted in a twin screw extruder where the reactants are brought together and substantially simultaneous reacted.

38. The process of claim 37 wherein said process is conducted at from about 110°C to about 200°C.

39. The process of claim 38 wherein the reaction time is from about 2 to about 3 minutes.

40. The process of claim 38 wherein said co-chain extender is used at a level of from about 5 to about 10 moles per 100 moles of said symmetrical chain extender.

41. The process of claim 40 wherein said polyether co-polyol is used at a level of from about 5 to about 20 parts by weight per 100 parts by weight of the total amount of said polyol.

42. The process of claim 35

A. wherein said polyester polyol is derived from an acid selected from the group consisting of adipic acid, suberic acid, sebacic acid, azelaic acid, and combinations thereof reacted with a glycol selected from the group consisting of 1,4-butanediol, diethylene glycol, 1,6-hexanediol, neopentyl glycol and combinations thereof;

B. wherein said polyether co-polyol is selected from the group consisting of poly(tetramethylene ether glycol), poly(ethylene oxide), poly(propylene oxide), poly(propylene oxide-co-ethylene oxide), and mixtures thereof;

C. wherein said polyisocyanate is a diisocyanate selected from the group consisting of MDI, H₁₂ MDI, and mixtures thereof;

D. wherein said symmetrical chain extender is selected from the group consisting of 1,6-hexanediol, 1,3-propanediol, 1,5-pentane diol, 1,4-butanediol, 1,4-

cyclohexanedimethanol, hydroquinone di(β -hydroxyethyl) ether, 1,4-benzenedimethylol, and mixtures thereof; and

E. wherein said co-chain extender is selected from the group consisting of 1,3-butanediol, neopentyl glycol, diethylene glycol, dipropylene glycol, di(β -hydroxyethyl) resorcinol, 1,2-propylene glycol, and mixture thereof.